Thematic Workshop A: "Operando Characterization of Energy Systems"
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In the study of energy systems such as batteries, fuel cells, photovoltaics, and catalytic processes, it is important to simulate their actual operating conditions as close as possible. This workshop brought together researchers engaged in operando studies of energy related systems to either highlight or stimulate studies exploiting the APS, CNM, and EMC.

Dean Miller of the EMC presented *in-situ* SEM investigations of the microstructural evolution of Li-ion battery cathode materials. A unique aspect is electrochemical measurements and microstructural characterization on isolated and individual oxide particles in cathode materials. Operando electron microscopic studies of single particles during cycling revealed dramatic changes in secondary particle microstructures such as cracking along grain boundaries even during the first cycle. These observations provide insightful explanations for the large changes in impedance during battery operation. Thomas Hansen from Denmark Technical University spoke about the use of environmental TEM (ETEM) in analyzing several energy-related systems including nanoparticle dynamics, photocatalysis, and nanoparticle-catalyzed alcohol synthesis. For example, the operando TEM studies with atomic resolution on a Ba-promoted Ru catalyst showed how *in-situ* TEM helps to understand catalyst activity. He also presented his recent work on obtaining information of the structure, composition and reactivity of photocatalysts with *in-situ* TEM. They combined conventional TEM analysis of photocatalysts with ETEM and photoactivation by introducing light through TEM sample holder. Two representative photo-induced processes were discussed: the photodegradation of Cu_2O and the photodeposition of Pt onto a GaN:ZnO photocatalyst.

The next two speakers were recipients of the 2011 DOE Office of Science Early Career Research Award for pioneering work in developing *in-situ* TEM techniques for probing nanocrystal growth and transformation in complex environments, including liquid solutions. Real-time probing of the complex chemical and physical events involved in nanocrystal growth and transformation is critical to help better understand the underlying mechanisms and, in turn, better synthesize nanomaterials with precisely tailored properties for applications with improved performance. Haimei Zheng from Lawrence Berkeley National Laboratory presented *in-situ* observations of single Pt_3Fe nanorod growth trajectories in solution using a specially designed TEM liquid cell. The atomic-resolution results revealed an evolution including multiple steps: i) the initial nucleation of Pt_3Fe nanoparticles in a molecular precursor solution; ii) growth into monodisperse nanoparticles; iii) nanowire formation by shape directed nanoparticle attachment; and iv) change of shape and crystal orientation to yield straight single crystalline Pt_3Fe nanorods. Shen Dillon from the University of Illinois at Urbana-Champaign (UIUC) showed the design of environmental TEM cells by incorporating varying environments that can provide external stimuli to drive nanocrystal growth and transformation. Typical examples include reactions in ionized gases and plasmas, reactions in solution, and electrochemistry. These in-situ capabilities enable new insights into dynamic phenomena with the unprecedented high spatial and temporal resolutions involved in the nucleation and growth of nanocrystals.

The afternoon session included a pair of talks about the operando investigation of heterogeneous catalysis with in-situ x-ray absorption spectroscopy (XAS) by Mathew Small from Ralph Nuzzo's group at UIUC. Matt showed the use of a new in-situ electrochemical XAS cell for studying the oxygen reduction reaction (ORR) mediated by nanoscale Pt electrocatalysts supported on carbon at high operating current densities. The results revealed a progressive evolution of the electronic structure of the metal clusters that is both potential- and current-dependent. Such understanding can help address a frontier challenge remaining in heterogeneous catalysis, i.e., how the atomic and electronic structural attributes of materials come to underpin the properties of complex heterogeneous catalytic systems. John Fulton from PNNL presented results for a number of catalytic systems under extreme conditions representative of industrial processes. He showed results for pressures of several hundred bars and temperatures of several hundred degrees (Celsius). Using small beams and diamond windows these measurements can be made for low energy edges such as Cl and Ca. At these conditions the state of the catalyst was found to be much different from their *ex-situ* state. An interesting example was presented for Rh based hydrogenation catalyst. From *ex-situ* studies this was thought to work heterogeneously through formation of Rh nanoparticles, but the *in-situ* work unequivocally found that the actual mechanism was homogenous through the formation of an Rh_4 molecular cluster.

Hector Abruna from Cornell followed with a lively talk about applying synchrotron methods to a variety of energy systems including batteries, supercapacitors, and fuel cells. Again he highlighted the importance of *in-situ* studies. His group has had some notable successes in applying XAS to the difficult case of sulfur-based battery systems. They have also been concentrating on the application of ordered intermetallics to the difficult problem of the oxygen reduction reaction in fuel cells.

The final talk was given by Mariana Bertoni from MIT about the application of x-ray microprobe methods to the investigation of defects in Si based solar cells. After an interesting introduction on the factors influencing the economics of solar cells, she described work using nanoscale x-ray beams to characterize metallic defects in polycrystalline solar cell material. This material is much less expensive to produce, but the performance is limited by these metallic defects. The insights gained through *in-situ* characterization at high temperature have allowed them to propose annealing procedures that can significantly reduce deleterious effects of the defects.